PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) Title: METHOD AND APPARATUS FOR THE CONTROL OF SOLIDIFICATION IN LIQUIDS

(57) Abstract

The invention provides a method of solidifying a liquid including the steps of reducing the temperature of the liquid below its melting point and subjecting the liquid to a physical disturbance, preferably irradiating the undercooled or partially solidified liquid with ultrasound to control nucleation and/or crystal growth. The preferred frequency of ultrasound is in the range 16-100 kHz, most preferably 20-40 kHz. In an embodiment of the invention undercooled liquids are irradiated at up to 1 °C below their melting point to induce formation of large crystals (500 microns) in the solidified product. In another embodiment partially solidified liquids are irradiated below their melting point so as to induce formation of many small crystals (50 microns) in the solidified product. Apparatus for carrying out the methods are described.

Title   Method and Apparatus for the Control of
         Solidification in Liquids

Field of the invention

This invention relates to a method of controlling
solidification of liquids. The term solidification as
used herein means the change in state from a liquid with
no bulk molecular ordering to a solid with a bulk
crystalline molecular structure.

The invention also relates to apparatus in which such
solidification processes can be carried out.

The liquids of interest include lipid and/or aqueous
systems (including solutions and emulsions) and other
systems which are fluid, under normal pressure, in the
temperature range -20° to 100°C.

The invention relates in particular to:

   (a) Freezing of foodstuffs which are normally
   consumed in the frozen state, including ice cream,
   frozen yoghurts, sorbets and ices.

   (b) Freezing of oil-in-water emulsions whose
   structure is irreparably damaged by freezing and
   thawing, eg. cream and various sauces.

- 2 -

(c) Production of foodstuffs and other consumer items having a high lipid content, such as cosmetics and polishes. In the case of foodstuffs, products may be entirely lipid (for example shortenings used in baking); or they may comprise a high proportion of lipid combined with sugar and other additives (for example chocolate and other similar confectionery); or they may be water-in-fat emulsions (for example margarines, halvarines, butter).

(d) Chemical processing of liquids, including for example freeze-concentration and fractionation including the dégorgement à la glace process in champagne manufacture.

(e) Crystallization of solutes in supersaturated solutions.

(f) Freeze drying or lyophilization is a process in which a sample is frozen, then a solvent (normally water) is removed from the frozen sample by sublimation. Currently many materials are freeze dried. These range from pharmaceuticals such as vaccines, antibiotics, industrial enzymes, fine chemicals etc to foodstuffs such as coffee, milk etc.

(g) Other foodstuffs with aqueous content.

Background to the invention

(A) The problem

It is a disadvantage with known methods of freezing liquids that some liquids once their temperature has been

- 3 -

reduced to below the melting point do not freeze, or do not freeze straightaway. Some liquids freeze into solids having an undesirable crystal form, or having an undesirable range and proportion of particular crystal sizes and orientation. In short it is difficult reliably to induce and/or control nucleation of liquids during freezing.

Solidification of liquids involves two processes - nucleation of crystals, followed by growth of those crystals to produce an ordered solid. There are several related problems associated with the solidification process:

1.   Initial nucleation. Many liquids have a strong tendency to supercool below their melting point before initial nucleation occurs. The consequent random nature of the nucleation limits the control of commercial solidification processes, including in polymorphic materials control of the polymorph formed.

2.   Crystal Growth. The crystalline structure of a solidifying melt is dependent on factors such as the density of nucleation sites, cooling rate, composition of phases present etc.

These nucleation/crystallisation phenomena lead generally to practical difficulties in controlling the solidification process and thus in producing solid products having particular desired characteristics, for instance:-

(a) The quality of products normally consumed in the

CID. <WO _ 9220420A1 I >

- 4 -

frozen state is largely determined by the size of
the ice crystals in the products. Those
containing large ice crystals are generally
considered to have poor customer acceptability.
It is desirable to manufacture ice cream which a
high proporation of ice crystals smaller than 55
micrometers diameter. Perceived coarseness in
ice cream is dependent upon the proportion of ice
crystals above this size, a higher proportion
resulting in a coarser taste. An additional
factor which determines
product quality is the sensitivity to ice
recrystallization during isothermal storage or
temperature abuse. Reducing the initial mean
crystal size and narrowing of the crystal
distribution will be beneficial.

(b) In oil-in-water emulsions such as single cream
     (typically about 18% fat content) and various
     sauces the formation of large ice crystals during
     freezing leads to a coagulation of the lipid
     content of the emulsion; on thawing the water and
     lipid remain separated. It is desirable to
     freeze these emulsions with small crystals so
     that the emulsions can be thawed with minimum
     separation.

(c) Shortenings are water free lipid products, the
     rheology of which depends on the solid fat
     content and the interactions between fat
     crystals. These crystals form a three
     dimensional lattice network (Juriaanse & Heertje,
     Food Microstructure 7, 181-188, 1988) and the
     commercially important characteristic, fat

- 5 -

hardness, is directly related to the
microstructure of the crystal lattice (Heertje et
al., Food Microstructure 7, 189-193, 1988). For
example, in puff pastry shortening a finer
crystal structure is preferred to a coarser
structure.

(d) In water-in-fat emulsions, such as margarines and
halvarines, the fat phase is continuous and the
method of nucleation/crystal growth determines
the product's consistency, firmness and microbial
stability (Juriaanse & Heertje, 1988; Heertje,
1988). Improved control over the nucleation and
crystal growth could allow the formulation of new
products.

(e) Cream is an oil-in-water emulsion which is
'ripened' for use in butter and ice cream
manufacture. The cream is held at reduced
temperatures to allow a proportion of the milk
fat in the cream globules to crystallize (the
Lipid Handbook, eds F.D. Gunstone, J.L. Harwood
& F.B. Padley, pp 224-225, Chapman & Hall,
London, 1986). To optimise this crystallization
a well defined temperature regime must be
applied, which depends strongly on the
composition of the milk fat, itself subject to
seasonal variations. Due to the problems
associated with nucleation of lipids, further
increased by the small globule size in cream, it
is necessary to hold milk at low temperatures for
several hours to ensure nucleation and crystal
growth.

- 6 -

(f) The quality of <u>chocolate products</u> is determined
    largely by the crystal form of triacylglycerols
    present in the chocolate. It is generally agreed
    that the preferred crystal structure is the beta
    form. However, complicated and time consuming
    processing steps are required to obtain chocolate
    containing the desired crystal form.

(g) Crystallization is also a commonly used method of
    chemical processing of liquids for example the
    <u>purification of fatty acids</u> and their derivatives
    (The Lipid Handbook. eds F.D. Gunstone, J.L.
    Harwood & F.B. Padley, pp 171-172, Chapman &
    Hall, London, 1986). In this case
    crystallization is either from the melt (dry
    fractionation) or from a solvent (solvent
    fractionation). 'Winterization', is a special
    case of fractionation deriving its name from the
    early practice of using cold winter weather to
    separate a solid fraction from cottonseed oil.
    The liquid fraction thus obtained does not suffer
    from unsightly deposits and does not cause
    emulsion separation on refrigeration of
    mayonnaise or salad dressings made from it.

    Another purification process, dewaxing, is used
    to remove naturally occurring waxes found in, for
    example, sunflower, safflower, corn and sesame
    oils (Ibid pp 213-215).

    In addition, freeze concentration of aqueous
    samples is employed when substances are either
    heat labile, for example in the production of
    orange and other fruit concentrates, or carry

- 7 -

health risks, for example radioactive compounds.

A special case is the dégorgement à la glace
process in champagne manufacture. The unwanted
yeast formed in secondary bottle fermentation is
collected at the neck by careful inversion of the
bottle. The neck is then placed in a freezing
bath and the yeast sediment is frozen into a plug
which is then removed.

To obtain good purification by separation,
crystals should be firm and of a uniform
spherical size ice crystals should be > 500
microns diameter for efficient filtration. If a
mass of very small crystals is formed, these are
difficult to separate by filtration.

(h) In <u>freeze drying</u> the freezing process influences
the size and shape of the ice crystals formed in
the sample and, therefore, the structure of the
porous solid that remains after drying. The
structure of the ice crystals determines the
characteristics of the sublimation step, and so
the freezing process also determines the time
required to complete the drying stages. It is
therefore desirable to control nucleation to
promote controlled solidification of samples. In
some cases it may be particularly desirable to
initiate freezing within a sample at or near its
melting point with a small number of large ice
crystals in the resulting frozen sample. In this
application we describe methods of controlling
nucleation in samples frozen outside the freeze
drying apparatus.

- 8 -

In co-pending patent application No. 9122617.5 is described the special case of nucleation of samples within a freeze drying chamber.

(B)   State of the art relating to the invention

1.   Nucleation in liquids below their melting point.

(a) Crystals of a number of chemicals are known to induce ice nucleation in supercooled water. These chemicals include silver iodide, various sterols, amino acids and 'ice nucleating' bacteria. Whilst the potential use of these substances has been suggested in various food applications, specifically ice creams, serious legislative problems will have to be overcome before their widespread use can be viable.

(b) In some processes, inoculants or 'seed crystals' of the appropriate type are added to a liquid to induce nucleation. This is a practice commonly employed in chocolate manufacture.

2.   Control of grain structure.

In other processes, inoculants or 'seed crystals of the appropriate type are added to a liquid to control grain structure.

(a) A number of additives are incorporated into ice creams and related products to limit the growth and recrystallisation of ice crystals. Products currently used include various gums, gelatin,

- 9 -

polysaccharides and other polymers.

(b) Naturally occurring inhibitors of crystal formation are removed from oils (Deffense E. & Tirtiaux A, J. Amer. Oil Chem. Soc., 60, 473).

(c) Nucleation and crystal growth of liquid products is usually carried out in scrape surface coolers. Scrape surface heat exchangers operate by seeding the bulk liquid with a large number of fine crystals. Margarines, shortenings and related products are now almost exclusively produced in multitube-cooler plants by a process known as the votator process (The Lipid Handbook, eds F.D. Gunstone, J.L. Harwood and F.B. Padley, pp 222-223, Chapman & Hall, London, 1986). Commercial ice cream processing employs an initial seeding step with freezing out of 50% of the available water in a sophisticated scrape surface cooler. Further freezing (hardening) is then completed in conventional blast freezers or tunnels. The texture of commercial ice creams is also largely affected by the incorporation of air, typically up to 50% by volume.

3. **Tempering to obtain a desired crystal polymorph.**

During chocolate processing a tempering step is used to ensure that the preferred beta crystal polymorph is formed and stabilised. Typically the polymorphic forms of chocolate have the following melting points:

    gamma form: 17°C

- 10 -

alpha form: 21-24°C
beta prime form: 27-29°C
beta form: 34-35°C

Tempering is carried out in specialised equipment in which molten chocolate (at about 45°C) is mixed to ensure an even temperature distribution. The temperature is then reduced to, say, 28°C, which is sufficiently supercooled to initiate nucleation. At this temperature the beta prime and beta crystal forms may co-exist. The temperature is then increased to, say, 30°C, above the melting points of any of the unwanted beta prime crystal forms, to allow crystal growth of the beta form.

Typically following tempering some 6-10% of the chocolate will be in the form of small beta crystals. In this form the chocolate is pourable and on further controlled cooling a stable product is produced.

Other tempering processes are employed during the cold ripening of cream for butter production, for example winter cream is kept for some hours in a tempering sequence at 8, 21 and 12°C according to the Alnarp method (The Lipid Handbook, eds F.D. Gunstone, J.L. Harwood & F.B. Padley, pp 224-225, Chapman & Hall, London, 1986). Also certain shortenings are stored above ambient temperature for a few days (Haighton, A.J., Fette Seifen Anstrichm., 65, 479-482, 1963), during which period a recrystallization process takes place in which mixed crystals "demix" and form other more stable crystals. This leads to larger crystals and slightly softer products.

- 11 -

According to the present invention there is provided a
method of solidifying a liquid, comprising the step of
subjecting the liquid to a physical disturbance to induce
vibration and/or cavitation in the liquid so as to control
the nucleation and/or crystal growth steps of the
solidification process.

The physical disturbance may be generated in many
different ways, for example by mechanical vibration or
stirring, oscillation or rotation, enhancement of natural
convection, electric fields, magnetic or electromagnetic
stirring, detonation and shock waves, vortices (however
produced), agitatin with gas bubbles, etc... However, the
preferred form of the disturbance is sonic or ultrasonic
vibration, most preferably ultrasonic.

Subjecting a liquid to a physical disturbance, including
vibration, during its solidification can modify both the
nucleation and the crystal growth stages of
solidification, depending on the stage in the
solidification process at which the disturbance is
applied. The modification is thought to be due to the
disturbance inducing "cavitation". Small bubbles of the
vapour phase of dissolved gas form out of a liquid as a
wave of disturbance passes through the liquid. These
bubbles collapse after the wave has passed, causing a
large pressure change which in turn induces nucleation in
the liquid. Since rate of nucleation is often a limiting
factor during solidification of a liquid, subjecting the
liquid to a physical disturbance so as to induce
cavitation, as in the present invention, can lead to
reduced solidification times.

- 12 -

This cavitation could also be achieved using hydro-dynamic
means such as a propeller or lifting surface so as to
create vortices in the liquid.

According to a first aspect of the present invention there
is provided a method of controlling the solidification of
a liquid, comprising the steps of reducing the temperature
of the liquid to below its melting point, and subjecting
the liquid to ultrasound so as to induce the nucleation
and/or crystal growth steps of the solidification
process.

One or more pulses of ultrasound can induce nucleation in
the liquid. This has the advantage that the initial
nucleation temperature of the liquid can be dictated.
This method also has the advantage that the technique is
chemically non-invasive. The use of vibrations, such as
ultrasound, is already an acceptable processing step in
certain treatments of foodstuffs, and thus use of the
present invention is not likely to encounter legislative
difficulties.

Since rate of nucleation is often a limiting factor during
solidification of a liquid, subjecting the liquid to
ultrasound so as to induce nucleation can lead to reduced
solidification times.

The preferred frequency of ultrasound is 16-100 KHz.
Above 100 KHz little nucleation can be obtained except at
extremely high power. The particularly preferred
frequency is between 20 and 40 KHz.

In an embodiment of the first aspect of the invention the
method comprises the step of subjecting the liquid to

- 13 -

ultrasound at a liquid temperature up to 1°C below its
melting point, preferably at between 0.25°C and 0.5°C
below its melting point.

The size of the ice crystals may be controlled by the
temperature at which the sample is treated, irradiating
slightly below the melting temperature will result in the
formation of a small number of large crystals in the final
product. This has an advantage in many applications, such
as freeze drying or fractionation, in which larger
crystals (>500 microns) result in a more efficient
process.

In a preferred embodiment of the first aspect of the
invention, the duration of applied ultrasound is up to 5
seconds, preferably up to 1 second. Prolonged application
of ultrasound can result in the formation of many
nucleation sites, which is not desired in the first aspect
of the invention as the object is to produce a few large
crystals in the solidified product.

In liquids where crystals already exist, new crystals may
be formed by fragmentation either due to cavitation or
other effects induced by the ultrasound, such as acoustic
streaming. This phenommenon is referred to as grain
refinement or grain multiplication.

In a second aspect of the invention a method of treating a
nucleated or at least partially solidified liquid
substance comprises the steps of maintaining the
temperature of the substance at below its melting point,
and subjecting the substance to ultrasound to reduce the
average crystal size in the solidifying liquid substance.

- 14 -

The preferred frequncies of ultrasound are as in the first
aspect of the invention. The ultrasound is preferably
applied continuously for at least 10 seconds, either in a
single pulse or preferably in a series of pulses of
shorter duration.

Irradiating a frozen liquid in this way results in a
reduction in crystal size which is of advantage e.g. in
ice cream manufacture where large ice crystals give a
coarse taste and in frozen emulsions where smaller
crystals enable a higher proportion of emulsion to be
recovered following freezing and melting of the emulsion.

For many applications the use of ultrasound will modify
simultaneously both nucleation and crystal growth.
However, these two phenomena may be controlled
independently in the invention by applying the disturbance
at appropriate different stages of the solidification
process. Generally, the ultrasound may be applied to the
liquid either before or during the solidification process
or following storage.

Ultrasonic vibrations may be generated by any convenient
means, in particular using electromagnetic, piezoelectric,
electrostrictive or magnetostrictive devices.

The ultrasonic power and frequency required will, in part,
be determined by the viscosity, temperature, pressure,
presence of solids and gas bubbles, dissolbed gas content
etc of the fluid to be treated. In general, the desired
ultrasonic conditions are those which will result in
cavitation within the bulk undercooled fluid to induce
nucelation or to cause grain refinement at a growing ice
front. This implies high intensity ultrasound which may

- 15 -

be generated most readily at the lower ultrasound
frequencies.

The efficiency of nucleation in a fluid which is
undercooled will be dependent on the extent of
undercooling and the density and distribution of the
cavitation sites within the fluid. To induce nucleation
in undercooled fluids ultrasonic power levels of >2 watts
per litre are preferred. The power levels required for
grain refinement are >1 watt per sq cm at the surface of
the liquid to be treated, preferably.

The sources of ultrasound may be coupled directly to the
liquid, but may also be connected indirectly via coupling
mechanisms such as horns, waveguides and/or through the
walls of a container holding the liquid.

The methods of the invention can easily be used in
conjunction with existing solidification processes or
appropriate stages in such processes, so as to enhance the
results achievable. The ultrasound is applied to the
liquid at an appropriate stage before or during a
solidification process, depending on whether nucleation or
crystal growth or both are to be modified. Generally, the
liquid will be cooled in conventional manner before,
during or after application of the ultrasound.

Overall, the method of the invention allows solidification
of many liquid systems, to be conducted more efficiently
and with greater control than was previously possible,
leading to a potential to produce better quality products
and even possibly new products.

In the present invention, the products to be treated are

- 16 -

all flowable liquids or droplets and the ultrasound may be
applied directly or indirectly from a transducer coupling
through the walls of vessels containing the liquids, via
stirrers or drive shafts, or by direct immersion of
ultrasonic probes in the liquids. The vessels and
stirrers commonly used in chemical and food processing are
generally made from stainless steel, which is a reasonably
good transmitter of ultrasonic vibrations.

For other applications, for example in freeze drying and
in champagne processing, the liquids are in glass
containers, which are also good transmitters of ultrasonic
vibrations.

The particular form of apparatus used to carry out the
methods of the invention will vary according to the liquid
to be solidified and will generally depend on the type of
apparatus normally used to solidify such liquids.
Conveniently, liquid cooling apparatus, modified to
include an appropriately positioned and suitably
controllable source of physical disturbance, can be
used.

The invention thus includes within its scope apparatus for
solidifying a liquid, comprising a source of ultrasound by
means of which the liquid can be subjected to ultrasound
so as to control the nucleation and/or crystal growth
steps of the solidification process.

The apparatus will typically take the form of a vessel
operating as a batch or continuous system in which the
liquid can be cooled to suitable temperatures. Various
embodiments of the invention are now described with
reference to the accompanying drawings in which:-

- 17 -

Figures 1a and 1b show schematic side views of a tube
resonator adapted to operate according to a second aspect
of the invention;

Figure 2 shows a schematic side view of a batch ice cream
maker adapted to operate according to a second aspect of
the invention;

Figure 3 shows a graph of crystal size distribution in a
frozen sucrose solution after treatment by a method
according to a second aspect of the invention, compared
with a control sucrose solution;

Figure 4 shows a graph of crystal volume distribution in
the solutions of Figure 3;

Figure 5 shows a photomicrograph of untreated margarine;

Figure 6 shows a photomicrograph of margarine which has
been melted and allowed to re-set; and

Figure 7 shows a photomicrograph of margarine which has
been melted and then ultrasonically treated according to a
second aspect of the invention on subsequent cooling and
re-setting.

1.   Continuous Processing

Continuous processing may be achieved by passing the
liquid or partially solidified liquid through an
ultrasonic flow cell provided that heat removal takes
place when solidification is required. The ultrasonic
flow cell may be a simple flow cell, a radial system, or a

- 18 -

cylindrical or flat plate reverberatory reactor. Such a
cylindrical or flat plate reactor should be driven close
to a mechanical resonant frequency.

The operating conditions will vary with liquid flow rate
and diameter of the flow cell. A simple way of continuous
processing would be to flow the cooled product through
conventional pipework which is passed through an
ulstrasonic bath which is maintained at a suitable
temperature. The ultrasonic power levels required would
be determined by the nature of the product to be treated
but would be at least 5 watts per litre coolant fluid
used. The ultrasonic frequency would be between 16-100
kHz with the preferred being 20-40 kHz.

A preferred apparatus for continuous liquid processing
according to a second aspect of the invention is a
midified tube resonator (Telsonis, Bronschofen,
Switzerland). In Figures 1a and 1b a tube resonator shown
generally at 1 has a head end 2 containing a piezo-
electric ultrasound generator. In operation the whole of
the surface 3 resonates at an ultrasonic frequency. Inlet
4 and outlet 5 are positioned at nodal points on the tube.
In Figure 1a one use of the tube resonator is shown in
which liquid to be processed in pumped into the inlet 4,
flows inside the tube resonator and emerges from outlet 5.
During this processing the resonating surface 3 is cooled
by any appropriate means. Alternatively, as shown in
Figure 1b, a suitable coolant may be pumped through the
tube resonator with product flowing in a concentric tube.
Product flows into the concentric tube through inlet 7,
flows through the space 8 defined by the housing 6 and the
resonator surface 3 and exits through outlet 9. A further
modification would be t use two concentric tube resonators

- 19 -

with coolant pumped through the inner tube, with product
flowing between th two resonators, the outer tube
resonator to be cooled by any appropriate means.

2.   Scrape Surface Coolers

In its simplest form, a scrape surface cooler is a
concentric tube heat exchanger in which the material in an
inner tube is externally cooled by a parallel or counter
flow of coolant in an outer tube. A steel rotor is fitted
with rows of scraper blades pressed against the cooled
inside surface of the inner tube. Liquid is processed in
a continuous manner and a flowable 'slush' is extruded for
further processing.

Using such equipment to carry out the method of the second
aspect of the invention, and in cases where the ultrasound
is to be applied by means of transducers, the ultrasound
is applied to the liquid in the cooler preferably through
the inner surface of the cooler. The application of
ultrasound to growing crystals results in grain refinement
or multiplication by fragmentation. In the scrape surface
heat exchanger the region of most rapid crystal growth is
near to the surface of the wall. Such positioning of the
acoustic source would appear to be most appropriate for
the generation of multiple seed crystals. As crystal
growth is occuring over the whole inner surface of the
scrape surface heat exchanger, maximum benefit would be
obtained by applying ultrasound over the whole processing
surface. The application of ultrasound at the surface may
also remove the requirement for mechanical scraping - ie
operate as an "acoustic scraper", this may simplify
design. In addition in such a configuration, any heat
generated by the transducers will be absorbed by the

CID: <WO   9220420A1 I >

- 20 -

coolant flow rather than by the liquid to be solidified.

In radial system, transducers may be mounted in a number
of configurations, such as:

(i)   Attached to the outside of the scrape surface cooler,
      with the disturbance being transmitted through the
      outer wall of the cooler, the coolant and finally the
      inner wall of the cooler. This configuration is
      potentially simple to fit to existing coolers to
      modify them for use in the invention, however
      significant power (for instance, acoustic power when
      the disturbance takes the form of sonic or ultrasonic
      vibrations) may be absorbed by the coolant.

(ii) The transducers are sealed through the outer wall and
      directly attached to the inner wall, optimally with
      The number, separation and distribution of
      transducers along the length of the scrape surface
      cooler should in any case be optimised for the
      particular material being solidified and the type of
      heat exchanger being used.

The disturbance may also be applied to the liquid via the
central drive shaft of the cooler or via a vibrating probe
positioned in the bulk of the liquid, or via a central
reverberatory cylinder. Care must be taken when
positioning a probe in a system with rotors, and account
also taken of heat generated by the transducers within
the liquid. In all cases, to achieve maximum benefit it
is necessary to cool the vibrating surface.

It will be understood that a combination of one or more of
the above configurations may also be of use in the methods

- 21 -

of the invention.

3.   Tempering Units (eg. for chocolate tempering)

As described above, chocolate is tempered either in small
batch systems or, more usually, by a continuous process.
Where the method of the invention is to be used to
nucleate chocolate in a batch system, the ultrasound could
either be applied through the wall of the tempering vessel
in a manner similar to that described for coolers above,
or transducer probe(s) could be placed directly in the
vessel.

In continuous systems the molten chocolate is pumped over
a series of scrape surface coolers. Transducers will
preferably be mounted within the scrape surface coolers in
the zone of the tempering unit at which the temperature of
the chocolate is such that beta crystals may be nucleated
(typically 32-34°C).

The ability to nucleate specifically at a temperature at
which beta crystals are formed, using the method of the
first aspect of the invention, removes the requirement for
tempering and this step may now be omitted in the
processing of chocolate products, allowing a more rapid
processing time.

4.   Moulds.

In moulded products such as some ices, sorbets, etc...,
the ultrasound may be applied either directly or
indirectly through the mould itself.

Many moulded products are manufactured by partial

SUBSTITUTE SHEET

- 22 -

immersion of the moulds on a conveyor belt through a
cooling fluid. In this case the ultrasound would be
transmitted through the cooling liquid and generated by
any suitable means. The ultrasonic frequency would be
between 16-100 kHz preferably 20-40 kHz and the power
levels required would be >5 watts per litre of cooling
fluid.

5.   Other Continuous Processes.

In the cold ripening or ageing of cream a batch process is
currently employed. The application of a physical
distrubance to assist solidification should allow the
development of continuous, hence more efficient,
processes. Following cooling to the appropriate
nucleation temperature, milk would be passed through, for
example, an ultrasonic flow cell. This may be a simple
flow cell, a radial system or a cylindrical or flat plate
reverberatory reactor.

Alternatively a "whistle" reactor, such as is used in the
manufacture of mayonnaise etc (inducing emulsification by
generating vibrations), may be employed. In this latter
case, the milk would be perturbed whilst flowing past a
vibrating edge or through an oscillating or rotating
aperture.

6.   Post Treatments.

Following either conventional liquid processing, or
processing in which ulltrasound has been applied, crystal
size in a product may be further modified by passing the
product through an ultrasonic flow cell or whistle
reactor. The operating conditions will again vary with

- 23 -

flow rate, diameter of the flow cell and product type.

7.   Freeze Drying.

The pre-freezing of relatively small volumes of high value
pharmaceuticals and fine chemicals for freeze drying is
often carried out in a low temperature bath. A consistent
quality of freeze-dried pharmaceuticals or chemicals
depends on being able to nucleate all samples at the same
temperature. Ultrasound may be applied through the
cooling fluid by suitably positioned transducers.

Ultrasound will be applied when the sample temperature is
typically up to 1°C below its melting point, and most
preferably between 0.25°C and 0.5°C below its freezing
point. The duration of the ultrasound is up to 5 seconds
and most preferably up to 1 seconds. Ultrasound is
applied to initiate nucleation at the required temperature
and not applied in a continuous manner to effect grain
refinement.

For large volumes of lower value products such as coffee,
an aqueous concentrate is frozen and then ground before
drying. The freezing process is controlled so that
regions of concentrated solution can develop due to the
growth of large ice crystals. The freezing methods
employed are either a "slow" method or a two step slow-
fast freezing process. Ultrasound may be used to produce
the desired ice crystal dimensions independently of the
cooling conditions employed. If large ice crystals are
desired, these may be produced by application of
ultrasound when the sample temperature is up to 1°C below
its melting point and most preferably between 0.25°C and
0.5°C below its freezing point. The duration of the

- 24 -

ultrasound is up to 5 seconds most preferably up to 1
second. Small ice crystals are produced by irradiating
the sample at greater levels of supercooling, ie up to 5°C
below its melting point, and/or by grain refinement of a
partially frozen solution.

8.   Ice Cream Manufacture.

Ice cream is manufactured in a modified scrape surface
cooler. However, a major difference to the other systems
described is that commercial ice creams contain a large
proportion (up to 50% by volume) of entrapped air.

Ultrasound is known to be effective indegassing solutions,
which in this case would modify the desired texture of the
ice cream product. This problem might be overcome by:

i)   Increasing the initial gas content such that the
      proportion lost as a consequence of ultrasonic
      irradiation or application of other physical
      disturbances will be compensated for.

ii)   Carrying out the process under increased pressure to
      reduce loss of any gas.

iii) Introducing the gas into the partially frozen
      product rather than at the beginning of the freezing
      process.

The tube resonator (described above) is especially
suitable for the continuous freezing of ice cream. The
resonator would be placed in line before the conventional
scrape surface heat exchanger. Ice cream mix cooled to
its freezing point would be pumped in, ice formation would

- 25 -

occur at the cold walls in any of the configurations
contained in Figures 1a and 1b. The continuous application
of ultrasound would ensure extensive grain refinement at
the growing ice front, resulting in the introduction of
multiple seed crystals into the conventional scrape
surface heat exchanger. This major advantage of the
apparatus is that it can simply be fitted in line without
major modification to the scrape surface heat exchanger.

Control.

(i)   Temperature sensors may be used to monitor the
       temperature of the liquid and to activate/control the
       source(s) of the physical disturbance. In this way
       the extent of supercooling may be specified,
       monitored and appropriately controlled.

(ii)   The attenuation of an acoustic signal by a fluid will
       be determined in part by the proportion of the fluid
       which has nucleated; this may provide a means of
       control of the solidification process. A separate
       system, to generate for example an ultrasonic signal
       and to measure its intensity at a distance or
       following reflection, may be used to control the
       characteristics of the disturbance used to initiate
       nucleation.

Alternatively the ultrasound source itself may be used for
control, by the appropriate positioning of an appropriate
receiver (for instance, an ultrasonic receiver).

One example of appropriate control would be in generating
the optimum amount of seed crystal in chocolate
manufacture. In other systems, following nucleation of

- 26 -

seed crystals the acoustic characteristics would be
switched to the optimum parameters for grain refinement.

Finally, information on the proportion of the system which
has nucleated could be used to control temperature,
especially in those applications which require tempering.

In some materials it is possible to induce nucleation of
too high a proportion of crystals for further processing.
For example with chocolate, excessive crystallization
during tempering makes the product highly viscous,
creating dosing and flattening problems. However,
irradiation by vibrations such as ultrasound will reduce
the effective viscosity in such a case, yielding a highly
crystallized, flowable material.

A suitable method of determining the proportion of
crystals in a fat is by ultrasonic means; therefore,
online measurements could be used to control nucleation
and crystal growth in fats and thus increase the
efficiency of the solidification process.

Example 1

Initiation of crystal growth in an oil. 10 ml
aliquots of commercial olive oil ("Extra Vergine",
available from Tesco), in glass universals, were
placed in a Fryka bath and cooled to -5°C. The oil
remained clear. The samples were then irradiated
with an acoustic probe (MSE ultrasonic disintegrator
Model 150W - 36 KHz). Following twenty 0.1 second
pulses of irradiation, there was little optical
evidence of crystal formation. However, when the
samples were returned to the bath at -5°C, after 15

- 27 -

mins the oil was uniformly opaque. All five
unirradiated samples, used as controls, remained
clear. Fatty acid analysis demonstrated that the
precipitate contained a higher proportion of
saturated fatty acids (23%) than the untreated sample
(13%). The supernatant was correspondingly enriched
with respect to unsaturated species.

Example 2.   Control of solidification of an Aqueous
             Solution

2.1   Description of the system. Referring to Figure 2, an
      Ariette batch ice cream maker shown generally at 20
      was modified to act as a low temperature ultrasonic
      bath which may be operated as a scrape surface
      freezer.

There are six transducers 21 (two shown) operating at
35kHz, frequency matched to two 100 watt generators
with controllable power output. Freon TF (Dupont) 22
was used as cooling fluid and for transmission of
ultrasound to the scraped surface. Cooling was of
the liquid being processed 25 achieved by venting the
exhaust from a pressurised liquid nitrogen vessel
through copper coils 23. In each batch experiment
300ml of the material was processed. Temperature was
monitored in the cooling fluid and in the sample
using T-type thermocouples (28 SWG) connected to a
data logger. The original scraper blades (not shown)
were driven at about 100 rpm to stir and scrape the
mix. Application of the ultrasound did not
significantly modify the temperature of the coolant
and as its temperature was reduced the efficiency of
the transmission through the Freon appeared to

- 28 -

increase.

2.2 <u>Analysis of Results</u>. Following cooling to -20°C
frozen materials were cut into slabs of approx 50x
50x10mm and immersed into liquid nitrogen. Samples
were stored in liquid nitrogen before sectioning on a
cold microtome followed by photography on a light
microscope with cold stage. The 35mm slides were
projected and crystals marked out in pen, these
outlines were then processed by image analysis to
produce data that can be presented as sizing bar
charts etc as discussed below.

i) <u>Unstirred</u>. Sucrose solutions (1.46M, freezing point
-2.66°C) were processed, unstirred, with the coolant
fluid maintained at -25°C. In the control, ie
unirradiated sample, large dendritic ice crystals
formed from the cold surfaces. In treated samples
ultrasound was pulsed into the system once ice was
observed to form at the cold wall. A pulse of
ultrasound of approximately 3 secs durations was
applied every 30 secs for 10 mins. The ultrasound
was clearly seen to fragment the ice front at the
cold wall and the crystal fragments were dispersed
into the bulk liquid. Following cooling to -20°C the
crystal structure was equiaxed. Compared with the
control sample the irradiated material was
mechanically harder.

ii) <u>Processed in the Scrape Surface Freezer</u>. The
application of ultrasound to a sucrose solution
(1.46M) during freezing to -5°C induced a shift in
the ice crystal size distribution compared with a
control preparation. The results are shown in Figure

- 29 -

3.   In the ultrasonically treated sample there was a
smaller mean crystal diameter, together with a
reduction in the percentage of crystals with a
diameter greater than 50 um, form 11.8% in the
control preparation to 4.4% in the ultrasonically
treated sample.   This shift in crystal distribution
is even more significant if the ice fraction is
calculated as a function of crystal size.   The
results are shown in Figure 4.   In the control, 55%
of the water exists in crystals of 50um or larger
compared to 33% in the ultrasonically treated
sample.

iii) <u>During Solidification</u>. The effect of ultrasound in
inducing grain refinement in partially solidified
solutions was examined following conventional
freezing of a sucrose solution (1.46M) to -5°C in a
scrape surface cooler, ultrasound was then applied
intermittently during subsequent solidification to -
20°C.   In this experiment the sucrose solution was
cooled to -20°C using the Ariette as a cooling bath
and with the scraper removed.   There was a reduction
in mean crystal size from 26um to 21um.   The
proportion of crystals with a mean diameter greater
than 45um reduced from 14% to 7%.

Example 3

<u>Initiation of the lipid phase change in margarine, a
water-in-oil emulsion</u>.   The effect of irradiation of
margarine with ultrasound during cooling was
determined in a stirred vessel.   300g of Flora
(Registered Trade Mark) margarine was placed in a
pyrex dish (115mm diameter) and melted using a water

bath at 50°C. The dish was then positioned in a
large tray containing alcohol to a depth of 50mm and
cooled to -2.5°C by a cooling coil through which
alcohol was pumped from a Fryka cooling bath. The
pyrex dish was positioned above a Stuart Scientific
stirrer SM1 and stirred using a 45mm magnetic flea at
speed setting 7.5. A lid was placed over the pyrex
dish, through which lid were placed thermocouples and
an acoustic probe. The thermocouples (28 s.w.g.)
were positioned 15, 35 and 55mm from the edge of the
dish, and were connected to a data logger (Grant
Instruments, Cambridge, 1200 series). The ultrasonic
probe (Lucas Dawe Ultrasonics, Model 250 Sonifier,
fitted with a tapered micro tip) was positioned 40mm
below the surface of the melted margarine.

Care was taken that the positioning of the acoustic
probe and the thermocouples, the cooling bath
temperature and the stirring rate were all constant
from experiment to experiment. The margarine was
irradiated with ultrasound, 25 x 0.1 second pulses at
30, 27.5, 25 and 20°C. When the sample had cooled to
10°C it was then transferred to plastic universals
for long-term storage at 20°C.

Margarine which had been melted and then allowed to
set remained semi-fluid on storage and was a brighter
yellow in colour than the original product. The
ultrasonically treated margarine was significantly
firmer than the untreated sample and was a paler
yellow, ie. in consistency and colour it remained
similar to the untreated product.

Light microscopy confirmed these differences. In

- 31 -

comparison with the original product (Figure 5), the product which had been melted and re-set (Figure 6) contained large water droplets, the solid lipid appearing as amorphous fat and spherulites, apparently suspended in an oil. In the product which had received the ultrasonic treatment (Figure 7) the water droplets were similar in size and distribution to those in the original product. As in the original product, the lipid appeared continuous with no evidence of a lipid phase separation, suggesting that co-crystallization of lipids had occurred.

Example 4

Control of freezing of oil-in-water emulsions: Single cream.

10 ml samples of commercially produced pasteurized single cream (approximately 19.3% fat content) were frozen in

   (i) A domestic freezer at -24°C

   (ii) A simulated scrape freezer cooled with a brine/ice water mixture at -19°C (sample cooling rate c. 20°C per min). The brine/ice mixture was contained in an ultrasonic cleaning bath (Kerry Model PVL55) which allowed sonication of the test liquid during freezing at a power density of c. $2kWm^{-2}$ (determined calorimetrically) at 38 kHz.

Comparison, with the starting material, of thawed samples previously frozen

(i) in glass phials in the domestic freezer
(ii) in the scrape freezer without ultrasound
(iii) in the scrape freezer continuously sonicated during freezing

showed the following:

In samples from (i) and (ii) the emulsion was broken, with lipid and aqueous components apparently completely separated. There was no obvious difference between the results of the two freezing regimes. In most samples from (iii) some very slight breaking of the emulsion was visible, in some samples, more; the extent appeared to be a function of the starting condition (age, supplier) of the cream. Gentle centrifuging of 50g of the thawed samples confirmed these qualitative conclusions:

Procedure (i) resulted in 40% (+/- 3%) of aqueous components separating;

Procedure (ii) 37% (+/- 4%);

Procedure (iii) 6.2% (+/- 1.5%), ie. superior results when the thawed emulsion was solidified using the method of the present invention.

Example 5

Control of ice crystal size for freeze drying

1 ml aliquots of a 1.2M sucrose solution (freezing point - 2.4°C) contained in glass freezing drying apoules were

- 33 -

cooled for 15 min in a low temperature bath maintained at
either -3.5°C or -7.5°C. Ice was nucleated by irradiation
for 5 seconds with ultrasound in an ultrasonic bath (Kerry
model PUL 55) containing water at 0°C, the samples were
then placed back into the low temperature bath for a
further 5 min. Following nucleation at low levels of
supercooling (1°C) a few large crystals were observed to
grow from a disc crystal into a stellar dendrite. In many
cases growth of a single ice crystal was observed. With
more extensive supercooling (5°C) a rapid solidification
of the system occurs with multiple nucleation sites and
small ice crystal size.

The samples were then cooled to -40°C on the shelves of a
freeze drier and then freeze dried. The resulting freeze
dried plugs differed significantly. The samples nucleated
near to the melting point (-3.5°C) had large pores, those
samples nucleated at a significant level of supercooling
(-7.5°C) had a finer pore structure clearly reflecting the
differences in the initial ice crystal structure. For
many applications a large pore size, which leads to
enhanced drying is desired.

These results demonstrate that ultrasound may be employed
to control ice crystal morphology in a sample for freeze
drying. Other methods of ice nucleation, ie the use of
crystals of silver iodide or the addition of "ice
nucleating bacteria" are not practical as they contaminate
the sample.

Example 6

Purification of a lipid by precipitation from a solvent

- 34 -

Crude Lanolin (Croda Chemicals LA 1715) was dissolved by
heating to 75°C in ethyl acetate (British Drug Houses) to
give a 25% w/v solution. Samples (100 ml in a Pyrex
beaker) were then cooled to +5°C by partial immersion in a
low temperature bath (Fryka) left for 15 minutes at 5°C
and centrifuged. Samples were irradiated with ultrasound
from an ultrasonic probe (Telsonics model UHG-300/SE-7-
300) operating at 36 KHz, one second pulse per minute.

In the irradiated sample a significantly larger
percipitate, 55% of total sample was formed than in the
control (40% of sample).

Example 7

Nucleation and grain refinement using a tube resonator

A tube resonator (Telsonic, 37kHz, 150 watt, length 297mm)
was modified by drilling holes at the nodal points
allowing flow of liquid inside the tube. This was cooled
by immersion in a low temperature alcohol bath (Fryka) and
the liquid to be processed suitably pre-cooled was pumped
through the resonator (see Figure 1a). The efficient
production fo a dense suspension of fine crystals has been
demonstrated for an aqueous solution of sucrose (1.46M,
Mpt -2.66°C) with a bath temperature of -25°C and for
olive oil with a bath temperature of -5°C.

We have also examined the arrangement of passing a coolant
through the resonator with the product flowing co-axially
on the outside of the resonator (Figure 1b). In a
prototype constructed with an outer tube of perspex. ice
formation and efficient grain refinement at the resonator
wall has been observed with a solution of sucrose (1.46M)
in this case the coolant liquid was at -10°C.

- 3·5 -

Claims

1.   A method of controlling the solidification of a
liquid comprsing the step fo subjecting the liquid to a
physical disturbance to induce vibration and/or cavitation
in the liquid soas to control the nucleation and/or
crystal growth steps of the solidification process.

2.   A method as claimed in claim 1 in which the physical
disturbance is sonic or ultrasonic energy.

3.   A method of controlling the solidification a liquid
as claimed in claim 2 comprising the steps of:

a)   reducing the liquid to a temperature below
      its melting point, and

b)   subjecting the liquid to sonic or ultrasound energy
      so as to induce nucleation.

4.   A method as claimed in claim 3 in which the frequency
of ultrasound is between 16 and 100 kHz.

5.   A method as claimed in claim 4 in which the frequency
of ultrasound is between 20 and 40 kHz.

6.   A method as claimed in any previous claim, comprising
the step of subjecting the liquid to ultrasound at a
liquid temperature up to 1°C below its melting point.

7.   A method as claimed in claim 6 comprising the step of
subjecting the liquid to ultrasound at a liquid
temperature between 0.25°C and 0.5°C below its melting

- 36 -

point.

8.   A method as claimed in any of claims 3 to 7 in which the ultrasound is applied for up to 5 seconds.

9.   A method as claimed in claim 8 in which the ultrasound is applied for up to 1 second.

10.   A method of controlling the solidification of a liquid as claimed in claim 2 comprising the steps of:

a)   maintaining the temperature of the liquid below its melting point, and

b)   subjecting the nucleated or at least partially solidified liquid to ultrasound or sonic energy to reduce the crystal size in the liquid.

11.   A method as claimed in claim 10 in which the frequency of ultrasound is between 16 and 100 kHz.

12.   A method as claimed in claim 11 in which the frequency of ultrasound is between 20 and 40 kHz.

13.   A method as claimed in any of claims 10 to 12 in which the ultrasound is applied for at least 10 seconds.

14.   A method as claimed in any of claims 10 to 13 in which the ultrasound is applied in a series of pulses.

15.   A method as claimed in any previous claim in which the liquid is a foodstuff e.g. ice cream, a foodstuff in emulsion form, chocolate, coffee, yoghurt.

- 37 -

16. A method of manufacture of chocolate in which molten chocolate at between 32°C and 34°C is irradiated with ultrasound so as to induce formation of beta form chocolate crystals.

17. Apparatus for performing the method as claimed in any of the previous claims comprising:

a)   a reservoir for a liquid substance;

b)   means for reducing the temperature of the liquid substance, and

c)   means for generating ultrasound.

18. Apparatus as claimed in claim 17 comprising a scrape surface cooler.

19. Apparatus as claimed in claim 17 comprising a tube resonator.

20. A method as claimed in any of claims 1 to 16 substantially as hereinbefore described.

21. Apparatus as claimed in any of claims 17 to 19 substantially as hereinbefore described with reference to the drawings.
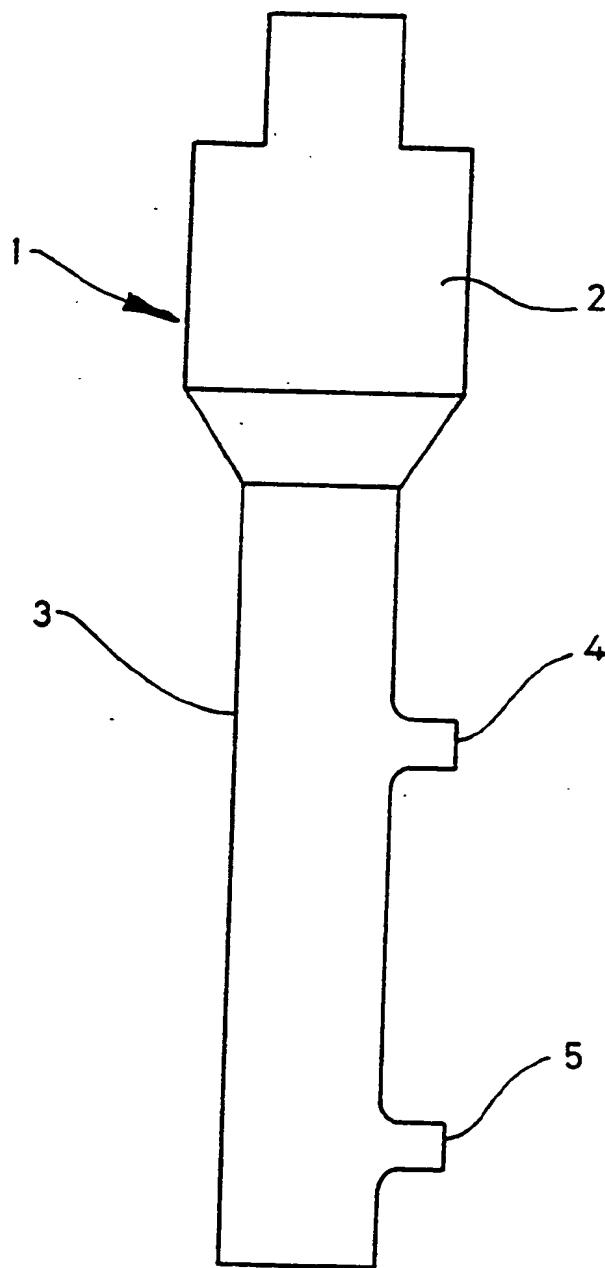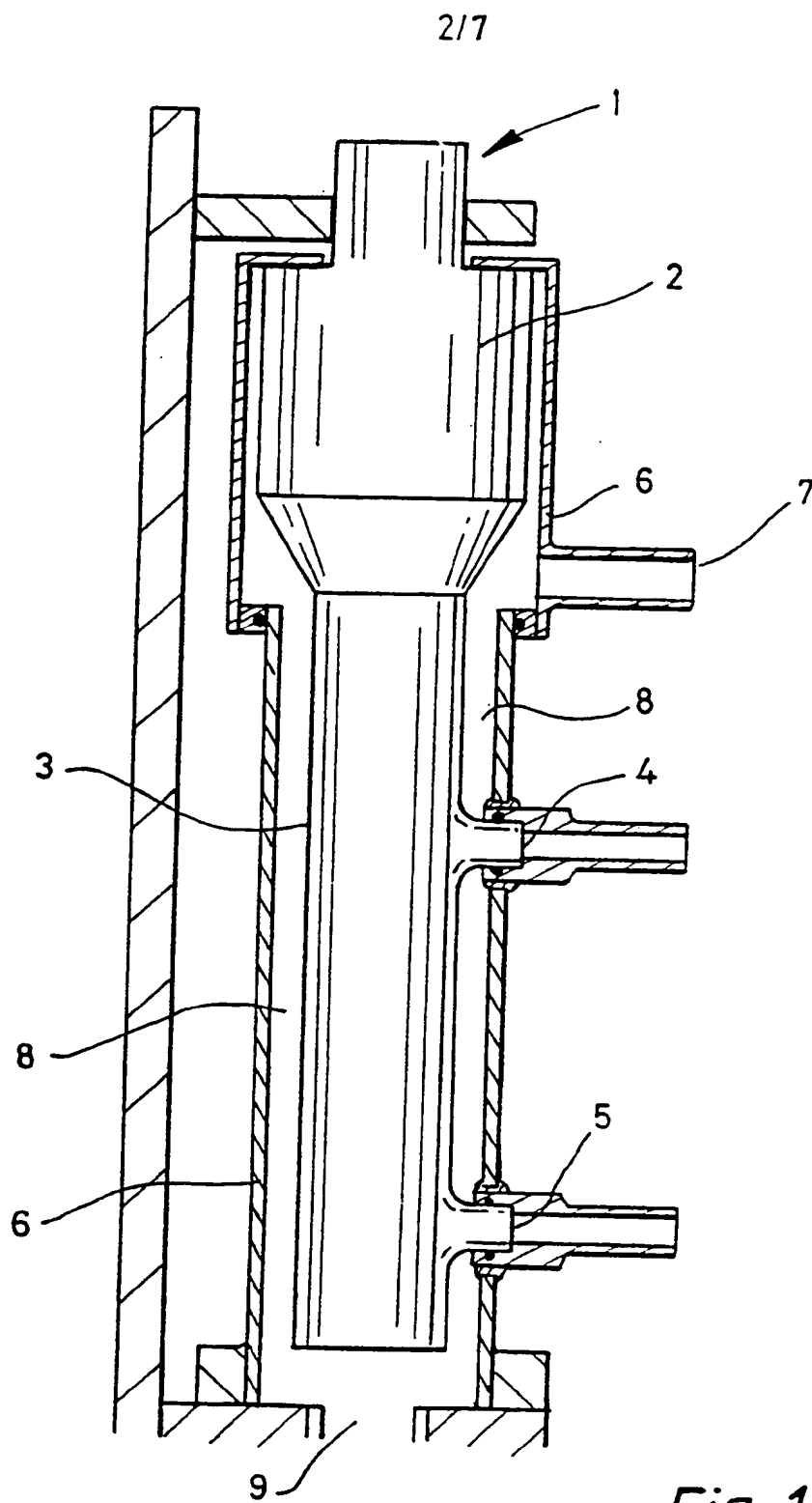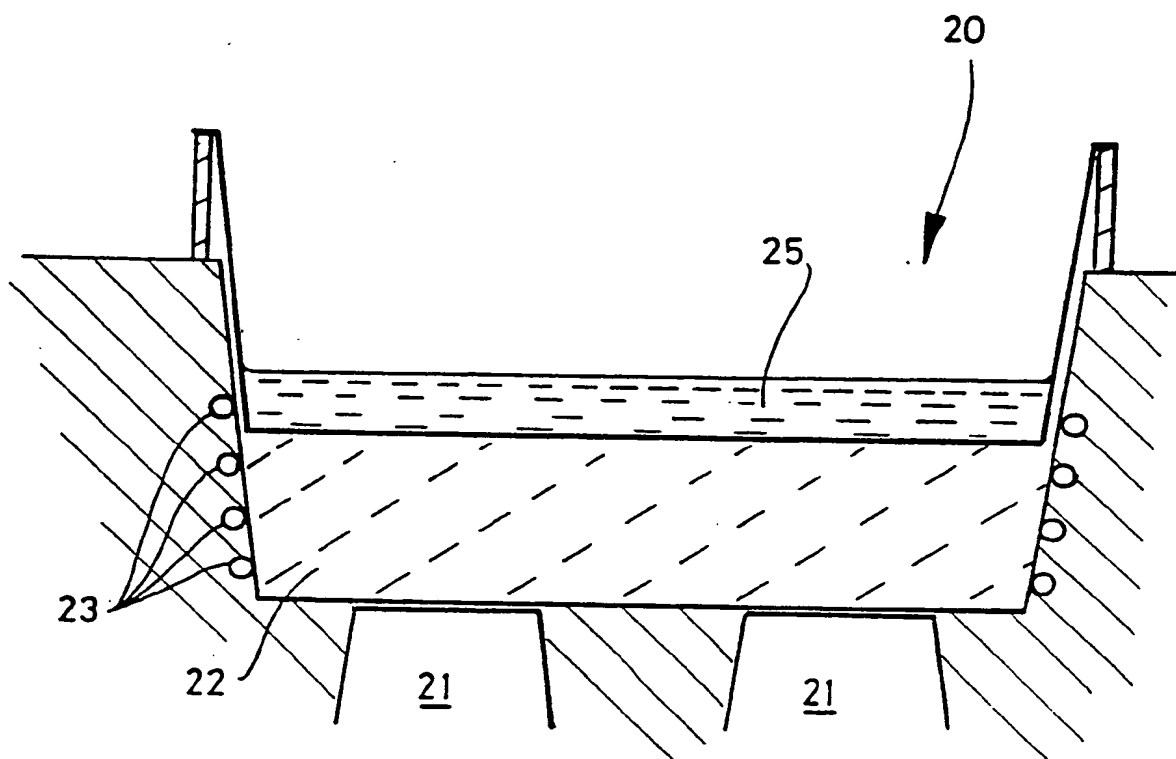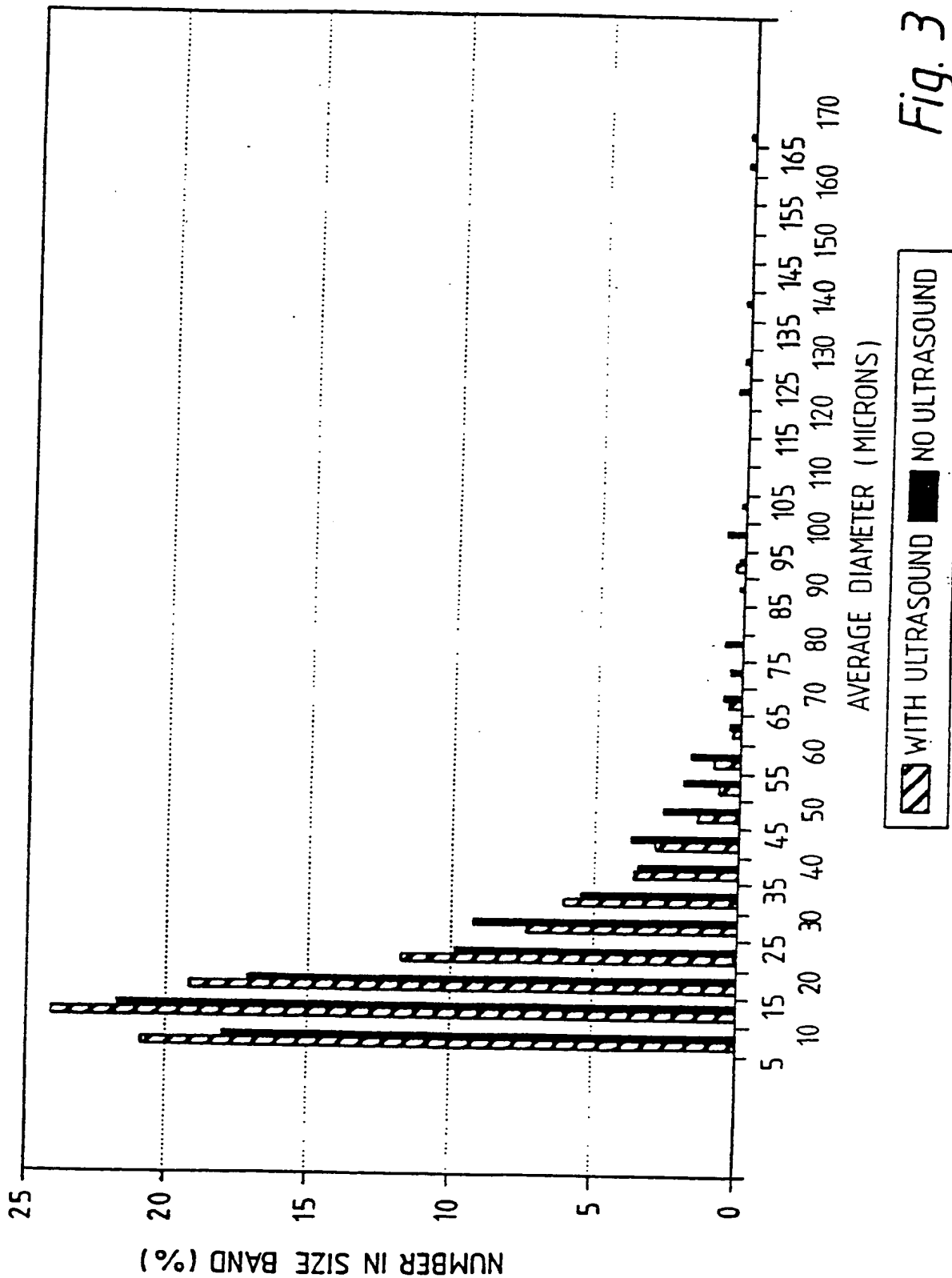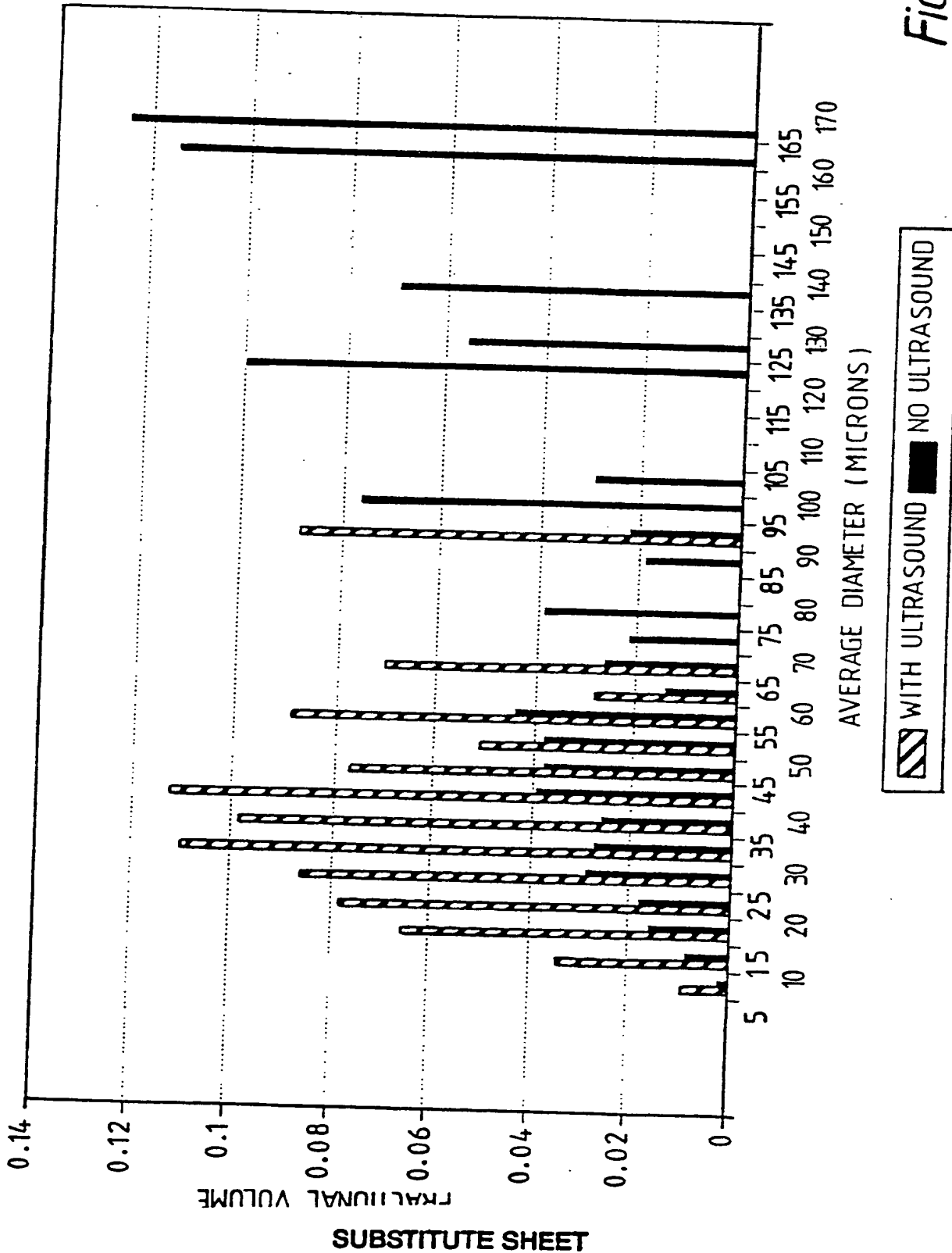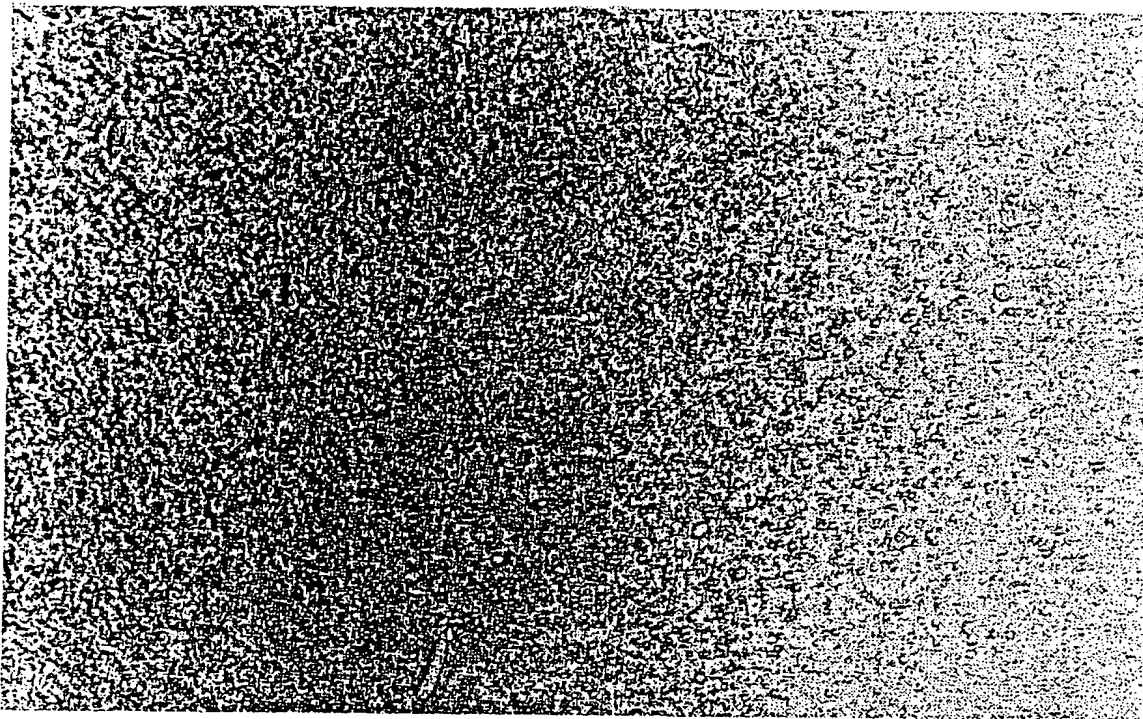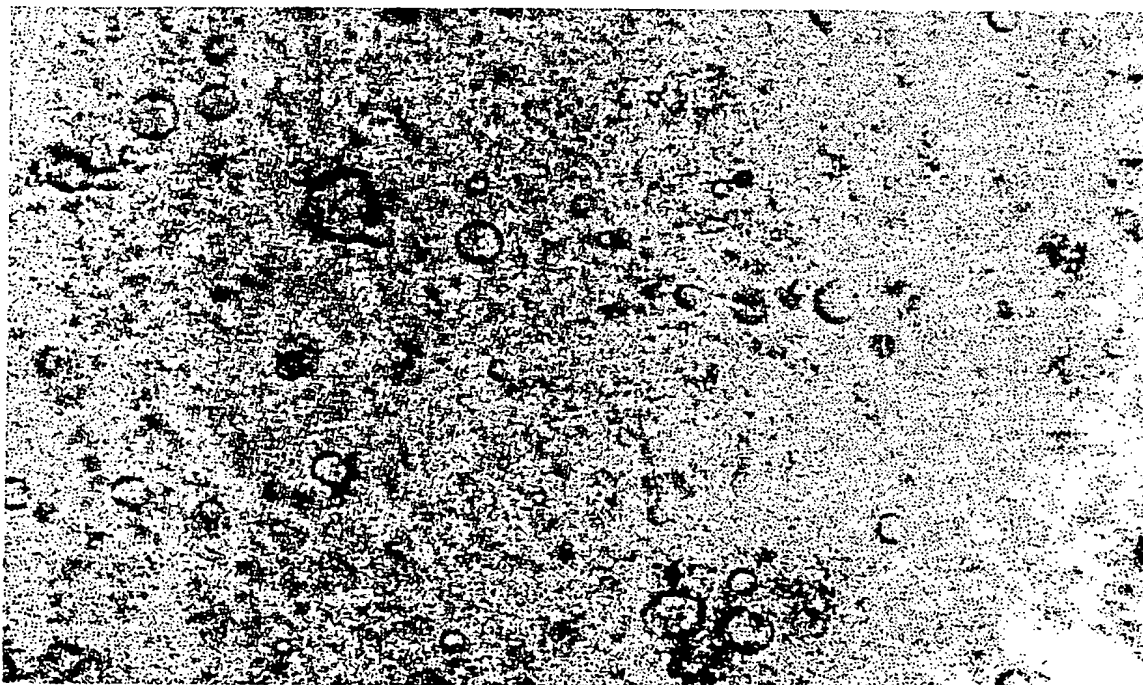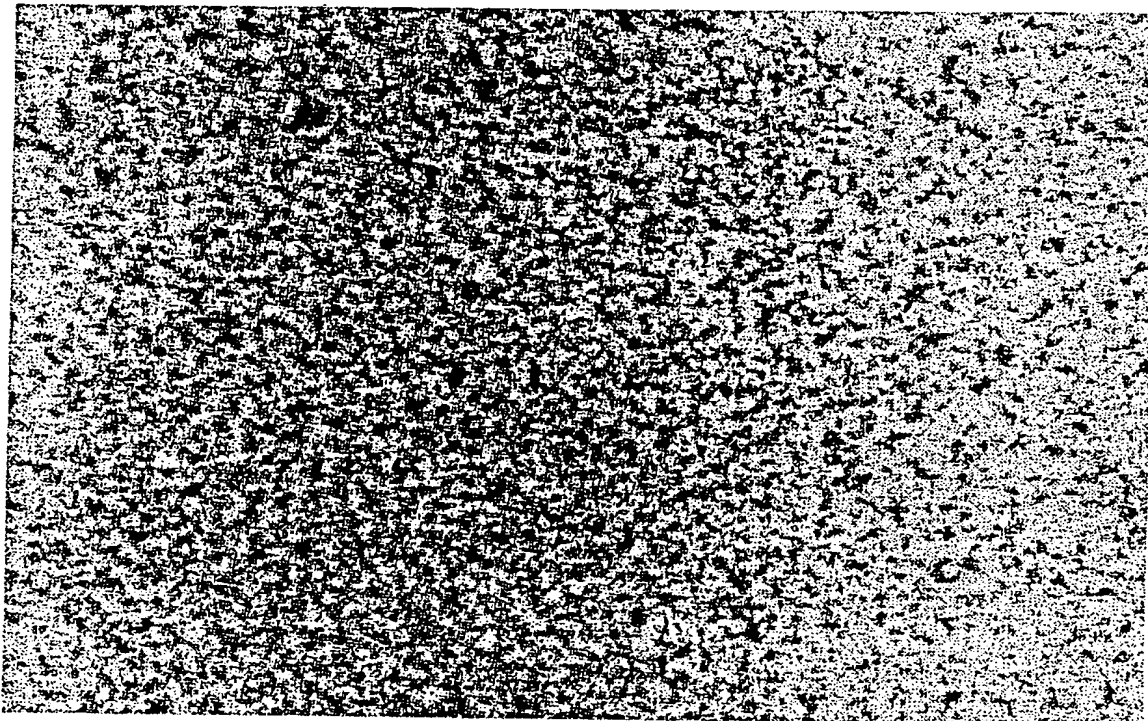
Fig.1a

Fig. 1b

CID: <WO___9220420A1_I_>

Fig. 2

4/7

Fig. 3

CID: <WO__9220420A1 I_>

5/7

Fig. 4

Fig. 5

Fig. 6

Fig.7

I. CLASSIFICATION OF SUBJECT MATTER   (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B01D9/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	B01D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	JOURNAL OF PHARMACEUTICAL SCIENCES. vol. 56, no. 11, November 1967, WASHINGTON US pages 1373 - 1385; D.M. SKAUEN: 'SOME PHARMACEUTICAL APPLICATIONS OF ULTRASONICS' CRISTALLIZATON see page 1377 - page 1379	1,2
Y	---	4,17,18
Y	SU,A,1 153 942 (VORON TECH INST.) 7 May 1985 see abstract; figure	4,17

Y	DE,A,840 389 (LINDE,S EISMASCHINEN A.G.) 17 April 1952 see claim 1	18

X	FR,A,1 099 427 (M. FRANZ PRIETL) 5 September 1955 see the whole document	1,2

	-/--	

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

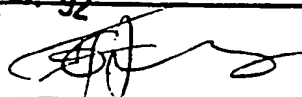| Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
17 JULY 1992	31. 07 92
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	PLAKA T.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category°	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	FR,A,1 418 859 (THE NOGUCHI INSTITUTE) 18 August 1965 see page D, left column, paragraph 1; claim 11	1,2

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. GB 9200818
SA 58974

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
SU-A-1153942	07-05-85	None	
DE-A-840389		None	
FR-A-1099427		BE-A- 521380 LU-A- 32263	
FR-A-1418859		US-A- 3450751	17-06-69